

A Model for the Oxidation of C/SiC Composite Structures

Roy M. Sullivan
Glenn Research Center, Cleveland, Ohio

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301-621-0134
- Telephone the NASA Access Help Desk at 301-621-0390
- Write to:
NASA Access Help Desk
NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076



A Model for the Oxidation of C/SiC Composite Structures

Roy M. Sullivan
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at <http://gltrs.grc.nasa.gov>

A Model for the Oxidation of C/SiC Composite Structures

Roy M. Sullivan
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Abstract

A mathematical theory and an accompanying numerical scheme have been developed for predicting the oxidation behavior of C/SiC composite structures. The theory is derived from the mechanics of the flow of ideal gases through a porous solid. Within the mathematical formulation, two diffusion mechanisms are possible: (1) the relative diffusion of one species with respect to the mixture, which is concentration gradient driven and (2) the diffusion associated with the average velocity of the gas mixture, which is total gas pressure gradient driven. The result of the theoretical formulation is a set of two coupled nonlinear differential equations written in terms of the oxidant and oxide partial pressures. The differential equations must be solved simultaneously to obtain the partial vapor pressures of the oxidant and oxides as a function of space and time. The local rate of carbon oxidation is determined as a function of space and time using the map of the local oxidant partial vapor pressure along with the Arrhenius rate equation. The nonlinear differential equations are cast into matrix equations by applying the Bubnov-Galerkin weighted residual method, allowing for the solution of the differential equations numerically. The end result is a numerical scheme capable of determining the variation of the local carbon oxidation rates as a function of space and time for any arbitrary C/SiC composite structure.

Introduction

The ability of carbon fiber-reinforced silicon carbide composites (C/SiC) to maintain its strength and stiffness at high temperatures as well as its low density make it an attractive candidate for many applications in future launch vehicles. These applications include turbomachinery components and thrust chambers in future propulsion systems as well as control surfaces, leading edges and thermal protection systems for vehicle airframes. One of the more formidable obstacles to the widespread use of C/SiC structures in future launch vehicles is that the carbon fibers oxidize at medium to high temperatures in an environment in which oxygen is present. This does not forbid the use of C/SiC in future launch vehicle applications, as long as it can be verified through testing and analysis that the component will maintain its strength and stiffness throughout its service life, with the demonstration of sufficient safety factors. As such, an assessment of the oxidation behavior of C/SiC composite structures must be included along with the usual design analysis activities such as the thermal, dynamic and thermostructural analysis of the component. It is therefore necessary to develop a tool that is capable of determining the spatial distribution of the extent of oxidation and the residual strength and stiffness in the C/SiC component as a function of the time, temperature and environmental oxygen concentrations to which the C/SiC structure is exposed. Currently, no such oxidation analysis tool is available to designers, who wish to utilize C/SiC composites.

Oxygen attacks the carbon in C/SiC composites both on the surface and in the interior of the composite. The oxygen achieves access to the interior of the composite via an interconnected pore network (Lamoureux, et al., 1993), which is formed by the combination of matrix cracks, separation of fibers from the pyrocarbon coating and void spaces between adjacent plies. The matrix cracks and fiber/coating separations are due to tensile stresses in the matrix, which are a result of the thermal expansion mismatch between the carbon fibers and the silicon carbide matrix in concert with the temperature excursions during processing and cool down. The large free spaces between plies are due to insufficient void filling during matrix infiltration. The porous nature of C/SiC composites is evident in fig. 1 where the microstructure of a 2-D C/SiC composite is shown. The oxidation of carbon in the interior of C/SiC composites is strictly tied to the transport of oxygen into and the transport of oxides out of the material. Any viable oxidation model for C/SiC composites must include the solution of species transport equations as the transport has a direct impact on the rate of carbon oxidation.

Oxidation models have been developed in the past in order to study the physics of the oxidation process in carbon fiber-reinforced composites. Medford (1975) proposed one of the earliest models. His approach was used to predict the oxidation performance of the Space Shuttle's carbon-carbon wing leading edge. His model attempted to simulate the diffusion of oxygen to the carbon-carbon substrate down a fissure in the SiC coating. He assumed steady state diffusion that was driven by oxygen concentration gradients across the coating thickness.

Eckel, et al. (1995) proposed a similar model to determine the oxidation recession rate of a carbon fiber embedded in a non-reactive matrix. The oxygen concentration distribution in a tubular pore was determined by the solution of a steady-state gas diffusion equation, which was derived assuming that the specie migration is a relative diffusion in a stationary gas mixture. The oxygen concentration adjacent to the carbon fiber surface and the temperature dictate the rate of carbon surface recession. Halbig (2001) adapted the model established by Eckel, et al. to simulate the fiber surface recession in C/SiC specimens. His approach presupposes a crack extending through the gage section bridged by an array of continuous carbon fibers.

Although these studies have provided insight into the physics of carbon oxidation in ceramic composites, these approaches are not readily applicable to support the design analysis of C/SiC structures as they are impractical for predicting the residual strength and stiffness as a function of space and time for any arbitrarily-shaped C/SiC structure. Indeed, these methods study the problem of carbon oxidation on a very fine scale, retaining the heterogeneous nature of C/SiC composites. As a result, these methods would be too cumbersome if they were applied to analyze C/SiC structures on a global level.

The purpose of this paper is to establish and develop an accurate analysis method to simulate the oxidation behavior of C/SiC composite structures in high temperature applications. In this paper, the mathematical theory that is the foundation of the method is presented. The theory is derived by assuming that the C/SiC material is a homogeneous, orthotropic porous body with a solid skeleton that is a mixture of multiple solid constituents where some of the constituents are reactive. The oxygen (oxidant) and the oxides (product) flow through the pore network and the partial pressures of the gases vary with space and time. Applying the fundamentals of porous media to this problem, namely the mass conservation equation for each gas specie as well as the transport mechanisms, a set of coupled, nonlinear differential equations is obtained. The Bubnov-Galerkin weighted residual method is used to cast the governing differential equations into matrix equations which allow us to solve the differential equations numerically.

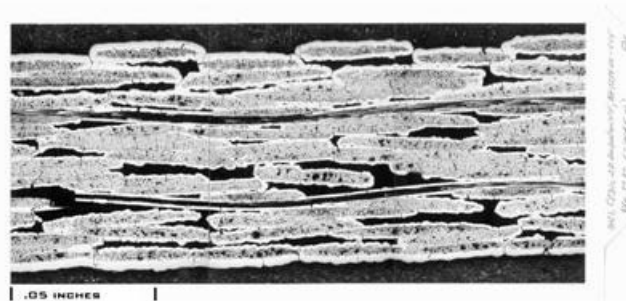


Fig. 1.— Optical Microscopy of 2-D C/SiC Composite.
(Courtesy of Southern Research Institute, Birmingham, AL)

Mathematical Theory

Mass Continuity for Flow Through Porous Media

In order to develop a mathematical theory to study the oxidation process, we make use of the basic principals of porous media theory, namely the equation for the continuity of mass of gaseous species flowing through a porous solid as well as mechanisms for transport in the porous solid. It is assumed that the oxygen and the products of the oxidation reaction (oxides) exist only in the pores of the material in a gas form and that these gases behave ideally, that the solid skeleton consists of a mixture of both silicon carbide and carbon in the solid form and that the carbon is oxidized at the interface between the solid skeleton and the pore, in other words, at the wall of the pore space.

The local form of the mass continuity equations for oxygen and the oxide species, flowing through a porous solid body, may be written as

$$\phi \frac{\partial \rho_{ox}^p}{\partial t} + \nabla \cdot \underline{\mathbf{J}}_{ox} = N_1 \frac{M_{ox}}{M_c} (\mathfrak{R}_{cf} + \mathfrak{R}_{pc}) \quad (1a)$$

and

$$\phi \frac{\partial \rho_{co}^p}{\partial t} + \nabla \cdot \underline{\mathbf{J}}_{co} = -N_2 \frac{M_{co}}{M_c} (\mathfrak{R}_{cf} + \mathfrak{R}_{pc}), \quad (1b)$$

respectively, where ϕ is the volumetric porosity, and where ρ_i^p is the local partial density in the pore volume, M_i is the molecular weight and $\underline{\mathbf{J}}_i$ is the local mass flux vector for specie i . The subscripts ox , co and c refer to the oxygen, the oxide (either carbon monoxide or carbon dioxide) and the carbon (solid form) species, respectively.

In equations (1a) and (1b), the symbols \mathfrak{R}_{cf} and \mathfrak{R}_{pc} denote the local time rate of carbon fiber mass and pyrocarbon coating mass consumption due to the oxidation reaction per unit bulk volume, respectively. Further, N_1 and N_2 are the stoichiometric constants for the oxidation reactions. That is, N_1 is the ratio of the number of moles of oxygen consumed in the oxidation reaction to the number of moles of carbon consumed in the reaction and N_2 is the ratio of the number of moles of oxide produced in the oxidation reaction to the number of moles of carbon consumed. As such, the right hand side (RHS) of (1a) is the local rate of oxygen mass consumed in the oxidation reaction per unit bulk volume and the RHS of (1b) is the local rate of oxide mass produced by the oxidation reaction per unit bulk volume.

In the oxidation of carbon, multiple reaction mechanisms are possible (Walker, et al., 1959). In this study, we will concentrate our attention on two mechanisms, which are denoted by the balance equations as



Thus, for Reaction A, $N_1 = N_2 = 1$, and for Reaction B, $N_1 = 1/2$ and $N_2 = 1$.

Upon substituting the ideal gas law for each specie i ($\rho_i^p = p_i M_i / RT$) into the first term in equations (1a) and (1b) and upon performing the differentiation, we obtain, after rearranging,

$$\phi \frac{M_{ox}}{RT} \frac{\partial p_{ox}}{\partial t} + \nabla \cdot \underline{J}_{ox} - N_1 \frac{M_{ox}}{M_c} (\Re_{cf} + \Re_{pc}) - \phi \frac{\rho_{ox}^p}{T} \frac{dT}{dt} = 0 \quad (2a)$$

and

$$\phi \frac{M_{co}}{RT} \frac{\partial p_{co}}{\partial t} + \nabla \cdot \underline{J}_{co} + N_2 \frac{M_{co}}{M_c} (\Re_{cf} + \Re_{pc}) - \phi \frac{\rho_{co}^p}{T} \frac{dT}{dt} = 0. \quad (2b)$$

Mass Flux Constitutive Relations

The mass flux of oxygen and the oxides through the pore network occurs via two mechanisms: gas pressure gradient-driven flow and concentration gradient-driven flow. That is, we may write the mass flux vector of specie i as the sum of two mass flux vectors as

$$\underline{J}_i = \underline{\bar{J}}_i + \underline{J}_i^{rel} \quad (3)$$

where $\underline{\bar{J}}_i$ is the mass flux associated with the average velocity of the gas mixture and is gas pressure gradient-driven and where \underline{J}_i^{rel} is the flux of specie i relative to the mixture average velocity and is concentration gradient-driven.

The expression for the gas pressure gradient-driven flow is attributed to Darcy (1856) and is written as

$$\underline{\bar{J}}_i = -\rho_i^p \frac{1}{\mu_g} \underline{k} \cdot \nabla p \quad (4)$$

where $\underline{\mathbf{k}}$ is the second-order material permeability tensor, μ_g is the viscosity of the gas mixture and p is the total gas pressure.

The concentration gradient-driven flow is given by modifying Fick's law (Bird, Stewart, and Lightfoot, 1960) as

$$\underline{\mathbf{J}}_i^{rel} = -\rho^p D_{AB} \underline{\Phi}^A \cdot \underline{\nabla} \left(\frac{\rho_i^p}{\rho^p} \right), \quad (5)$$

where ρ^p is the local gas mixture density in the pore and D_{AB} is the diffusivity of gas specie A with respect to gas specie B, and $\underline{\Phi}^A$ is the second-order areal porosity tensor.

Making use of the ideal gas law for each specie i ($\rho_i^p = p_i M_i / RT$) as well as the ideal gas law for the mixture ($\rho^p = p M_g / RT$), we can rewrite equation (5) as

$$\underline{\mathbf{J}}_i^{rel} = -\rho^p D_{AB} \frac{M_i}{M_g} \underline{\Phi}^A \cdot \underline{\nabla} \left(\frac{p_i}{p} \right), \quad (6)$$

in order to write (5) in terms of the partial pressure p_i . In (6), M_g is the molecular weight of the gas mixture.

Substituting equations (4) and (6) into (3) leads to

$$\begin{aligned} \underline{\mathbf{J}}_{ox} = & -\rho_{ox}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{ox} - D_{AB} \frac{M_{ox}}{RT} \frac{p_{co}}{p} \underline{\Phi}^A \cdot \underline{\nabla} p_{ox} \\ & - \rho_{ox}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{co} + D_{AB} \frac{M_{ox}}{RT} \frac{p_{ox}}{p} \underline{\Phi}^A \cdot \underline{\nabla} p_{co} \end{aligned} \quad (7a)$$

and

$$\begin{aligned} \underline{\mathbf{J}}_{co} = & -\rho_{co}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{co} - D_{AB} \frac{M_{co}}{RT} \frac{p_{ox}}{p} \underline{\Phi}^A \cdot \underline{\nabla} p_{co} \\ & - \rho_{co}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{ox} + D_{AB} \frac{M_{co}}{RT} \frac{p_{co}}{p} \underline{\Phi}^A \cdot \underline{\nabla} p_{ox}. \end{aligned} \quad (7b)$$

In the derivation of equations (7a) and (7b), it was necessary to employ Dalton's law for the gas mixture, ($p = p_{ox} + p_{co}$), the distributive property of the gradient operator ($\underline{\nabla} p = \underline{\nabla} p_{ox} + \underline{\nabla} p_{co}$) and the ideal gas law for the gas mixture.

It is apparent that, upon substituting equations (7a) and (7b) into (2a) and (2b), we will arrive at two coupled nonlinear differential equations written in terms of the partial pressures. These equations will be coupled, since terms involving the gradients ∇p_{ox} and ∇p_{co} will appear in both equations. These equations will be nonlinear, since (7a) and (7b) contain terms that involve the product of the partial densities and the gradients of the partial pressures as well as terms that involve the product of the partial pressures and the gradients of the partial pressures. The two nonlinear differential equations must be solved simultaneously at each time step to obtain the partial pressures at each spatial location. In the following sections, we present the numerical approach to achieve the simultaneous solution of these equations.

Determination of Oxidation Reaction Rates

The time rate of the carbon oxidation reaction is a function of the absolute temperature and the vapor pressure of the oxidant (Gulbransen, et al., 1963). The dependence of the reaction rate on temperature and pressure is usually modeled using the Arrhenius rate equation of the form

$$\frac{d}{dt} \left(\frac{m_c}{m_c^o} \right)_{\text{oxidation}} = -k_o \exp \left(\frac{-E_a}{RT} \right) p_{ox}^n \quad (8)$$

where m_c and m_c^o are the instantaneous carbon mass and the initial carbon mass, respectively, and where k_o is the pre-exponential coefficient, E_a is the activation energy of the oxidation reaction and n is the order of the reaction. The Arrhenius constants k_o , E_a and n are obtained by curve fitting thermogravimetric analysis (TGA) measurements to equation (8). Thermogravimetric analysis is performed separately on the individual carbon constituents (carbon fibers and the carbon coating).

As we are concerned with a solid mixture containing carbon, then for any unit volume of material, we can replace the mass ratio in (8) with a density ratio and equation (8) can be written as

$$\left(\frac{d\rho_c}{dt} \right)_{\text{oxidation}} = -\rho_c^o k_o \exp \left(\frac{-E_a}{RT} \right) p_{ox}^n \quad (9)$$

where ρ_c and ρ_c^o are the instantaneous mass density and initial mass density of carbon in the mixture, respectively.

In applying equation (9), it is necessary to recognize a few key differences between the oxidation of carbon fibers or pyrocarbon coating in TGA tests and the

oxidation of these constituents in C/SiC composites. First, the ambient partial pressure of oxygen in the TGA experiments is constant and specified as a test condition, whereas the oxygen partial pressure in the C/SiC composite varies with time and spatial location. Second, the carbon surface area that is exposed to oxygen vapor may be approximated as close to 100 percent in the TGA experiments, whereas this surface area fraction in the C/SiC composite is considerably less than this estimate and also varies as a function of time and spatial location. Furthermore, we note that by definition, $\Re_{cf} \equiv (d\rho_{cf}/dt)_{oxidation}$ and $\Re_{pc} \equiv (d\rho_{pc}/dt)_{oxidation}$, where ρ_{cf} and ρ_{pc} are the mass of carbon fiber and mass of pyrocarbon coating per unit bulk volume of material, respectively. Given these considerations, equation (9) may be rewritten separately for both the carbon fibers and pyrocarbon coating, as

$$\Re_{cf} = -\rho_{cf}^o \left(\frac{p_{ox}}{p_{ox}^*} \right)^{n_{cf}} \psi^{cf} k_o^{cf} \exp\left(\frac{-E_a^{cf}}{RT} \right) \quad (10a)$$

and

$$\Re_{pc} = -\rho_{pc}^o \left(\frac{p_{ox}}{p_{ox}^*} \right)^{n_{pc}} \psi^{pc} k_o^{pc} \exp\left(\frac{-E_a^{pc}}{RT} \right), \quad (10b)$$

respectively, where k_o^{cf} , E_a^{cf} and n_{cf} are the Arrhenius constants associated with the carbon fiber oxidation and k_o^{pc} , E_a^{pc} and n_{pc} are the Arrhenius constants associated with the pyrocarbon coating oxidation. The quantity p_{ox}^* is the ambient oxygen vapor pressure in the TGA experiments in which the values of the Arrhenius constants were determined.

Furthermore, in equations (10), we have introduced ψ^{cf} and ψ^{pc} as the fraction of the fiber surface area and fraction of pyrocarbon coating surface area that is exposed to oxygen in the composite material. It should be noted that ψ^{cf} and ψ^{pc} will be a function of time and the spatial location as it will depend on the temperature, the stress state and the degree to which the carbon is oxidized. We will leave the determination of the functional dependence of the surface area fractions on the temperature, the stress state and the degree of oxidation as the subject of future studies.

Assuming the density of carbon fiber and pyrocarbon coating are approximately the same, the relation between the densities and the volume fractions are $\rho_{cf} = \tilde{\rho}_c v_{cf}$ and $\rho_{pc} = \tilde{\rho}_c v_{pc}$, where $\tilde{\rho}_c$ is the density of pure carbon, v_{cf} is the volume fraction of carbon fiber and v_{pc} is the volume fraction of pyrocarbon coating in the composite. Therefore, equation (10a) and (10b) may be written

$$\mathfrak{R}_{cf} = -\tilde{\rho}_c v_{cf}^o \left(\frac{p_{ox}}{p_{ox}^*} \right)^{n_{cf}} \psi^{cf} k_o^{cf} \exp\left(\frac{-E_a^{cf}}{RT} \right) \quad (11a)$$

and

$$\mathfrak{R}_{pc} = -\tilde{\rho}_c v_{pc}^o \left(\frac{p_{ox}}{p_{ox}^*} \right)^{n_{pc}} \psi^{pc} k_o^{pc} \exp\left(\frac{-E_a^{pc}}{RT} \right), \quad (11b)$$

where v_{cf}^o and v_{pc}^o are the initial values of the volume fractions.

Finite Element Formulation

We now seek a method to solve equations (2a) and (2b) numerically to obtain the spatial distribution of the partial pressures for any arbitrary body at discrete times over any arbitrary time domain. We employ the Bubnov-Galerkin finite element method to cast the differential equations into a matrix form in order to perform the solution numerically. In addition, we note that the nonlinear differential equations must be linearized within each time step and solved over the time domain in a piecewise linear manner.

Applying the Bubnov-Galerkin method (Bathe, 1982), the finite element form of (2a) and (2b) are

$$\int_{D^e} N_i \{LHS_of_equ.(2a)\} dD^e = 0, \quad (12a)$$

and

$$\int_{D^e} N_i \{LHS_of_equ.(2b)\} dD^e = 0 \quad (12b)$$

where D^e is the domain of each element and where N_i are the element shape functions.

For the numerical solution of equations (2a) and (2b), we replace the variables p_{ox} , p_{co} , \mathfrak{R}_{cf} and \mathfrak{R}_{pc} with the approximations \bar{p}_{ox} , \bar{p}_{co} , $\bar{\mathfrak{R}}_{cf}$ and $\bar{\mathfrak{R}}_{pc}$, given by

$$\bar{p}_{ox}(x, y, z, t) = N_i(x, y, z) p_{ox_i}(t) \quad (13a)$$

$$\bar{p}_{co}(x, y, z, t) = N_i(x, y, z) p_{co_i}(t) \quad (13b)$$

$$\bar{\mathfrak{R}}_{cf}(x, y, z, t) = N_i(x, y, z) \mathfrak{R}_{cf_i}(t) \quad (13c)$$

and

$$\overline{\mathfrak{R}}_{pc}(x, y, z, t) = N_i(x, y, z) \mathfrak{R}_{pc_i}(t) \quad (13d)$$

where p_{ox_i} and p_{co_i} are the element nodal values for the oxygen vapor pressure and oxide vapor pressure, respectively, and where \mathfrak{R}_{cf_i} and \mathfrak{R}_{pc_i} are the element nodal values for the rate of carbon fiber mass and pyrocarbon mass consumption due to oxidation per unit bulk volume, respectively. Therefore, using equation (12a), (12b), and (13a) through (13d) and noting that the shape functions are not a function of the time variable, the finite element form of equations (2a) and (2b) become

$$\int_{D^e} N_i \phi \frac{M_{ox}}{RT} N_j \frac{\partial p_{oxj}}{\partial t} dD^e + \int_{D^e} N_i \nabla \cdot \underline{\mathbf{J}}_{ox} dD^e \quad (14a)$$

$$- \int_{D^e} N_i N_1 \frac{M_{ox}}{M_c} N_j (\mathfrak{R}_{cfj} + \mathfrak{R}_{pcj}) dD^e - \int_{D^e} N_i \phi \frac{\rho_{ox}^p}{T} \frac{dT}{dt} dD^e = 0$$

and

$$\int_{D^e} N_i \phi \frac{M_{co}}{RT} N_j \frac{\partial p_{coj}}{\partial t} dD^e + \int_{D^e} N_i \nabla \cdot \underline{\mathbf{J}}_{co} dD^e \quad (14b)$$

$$+ \int_{D^e} N_i N_2 \frac{M_{co}}{M_c} N_j (\mathfrak{R}_{cfj} + \mathfrak{R}_{pcj}) dD^e - \int_{D^e} N_i \phi \frac{\rho_{co}^p}{T} \frac{dT}{dt} dD^e = 0.$$

Using the Product Rule of differentiation along with Gauss' Theorem (Burnett, 1987), the second term in equations (14a) and (14b) can be expanded as

$$\int_{D^e} N_i \nabla \cdot \underline{\mathbf{J}}_{ox} dD^e = \oint_{\Gamma^e} N_i \underline{\mathbf{J}}_{ox} \cdot \underline{\mathbf{n}} d\Gamma^e - \int_{D^e} \nabla N_i \cdot \underline{\mathbf{J}}_{ox} dD^e \quad (15a)$$

and

$$\int_{D^e} N_i \nabla \cdot \underline{\mathbf{J}}_{co} dD^e = \oint_{\Gamma^e} N_i \underline{\mathbf{J}}_{co} \cdot \underline{\mathbf{n}} d\Gamma^e - \int_{D^e} \nabla N_i \cdot \underline{\mathbf{J}}_{co} dD^e \quad (15b)$$

where Γ^e is the boundary of the element and, as indicated, the integration is performed in a closed path around the element boundary. The boundary integral terms in equations (15a) and (15b) allow for the application of unconstrained boundary conditions (Burnett,

1987). These integral terms are only nonzero for elements where mass flux boundary conditions are imposed.

Substituting equation (7a) and (7b), equations (15a) and (15b) are written

$$\begin{aligned}
\int_{D^e} N_i \underline{\nabla} \cdot \underline{\mathbf{J}}_{ox} dD^e &= \oint_{\Gamma^e} N_i \underline{\mathbf{J}}_{ox} \cdot \underline{\mathbf{n}} d\Gamma^e + \int_{D^e} \underline{\nabla} N_i \cdot \rho_{ox}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{ox} dD^e \\
&+ \int_{D^e} \underline{\nabla} N_i \cdot D_{AB} \frac{M_{ox}}{RT} \left(\frac{p_{co}}{p} \right) \underline{\Phi}^A \cdot \underline{\nabla} p_{ox} dD^e + \int_{D^e} \underline{\nabla} N_i \cdot \rho_{ox}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{co} dD^e \\
&- \int_{D^e} \underline{\nabla} N_i \cdot D_{AB} \frac{M_{ox}}{RT} \left(\frac{p_{ox}}{p} \right) \underline{\Phi}^A \cdot \underline{\nabla} p_{co} dD^e
\end{aligned} \tag{16a}$$

and

$$\begin{aligned}
\int_{D^e} N_i \underline{\nabla} \cdot \underline{\mathbf{J}}_{co} dD^e &= \oint_{\Gamma^e} N_i \underline{\mathbf{J}}_{co} \cdot \underline{\mathbf{n}} d\Gamma^e + \int_{D^e} \underline{\nabla} N_i \cdot \rho_{co}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{co} dD^e \\
&+ \int_{D^e} \underline{\nabla} N_i \cdot D_{AB} \frac{M_{co}}{RT} \left(\frac{p_{ox}}{p} \right) \underline{\Phi}^A \cdot \underline{\nabla} p_{co} dD^e + \int_{D^e} \underline{\nabla} N_i \cdot \rho_{co}^p \frac{1}{\mu_g} \underline{\mathbf{k}} \cdot \underline{\nabla} p_{ox} dD^e \\
&- \int_{D^e} \underline{\nabla} N_i \cdot D_{AB} \frac{M_{co}}{RT} \left(\frac{p_{co}}{p} \right) \underline{\Phi}^A \cdot \underline{\nabla} p_{ox} dD^e.
\end{aligned} \tag{16b}$$

In order to linearize equations (16a) and (16b), we treat the partial pressures which are operated on by the gradient operator as the solution variables and assume that the partial densities and the partial pressures in brackets in (16a) and (16b) are constant within the element over the duration of any arbitrary time step. Therefore, the partial pressures in brackets and the partial densities may be taken outside the volume integral and the gradient terms $\underline{\nabla} p_{ox}$ and $\underline{\nabla} p_{co}$ are replaced with the approximations $\underline{\nabla} N_i p_{ox_i}$ and $\underline{\nabla} N_i p_{co_i}$.

Furthermore, we assume that the temperature, the gas viscosity, the diffusivity and the volumetric porosity are all constant within the element (although these quantities may vary from element to element) and therefore these quantities may be taken outside the volume integrals in equations (16a) and (16b).

After substituting equations (16a) and (16b) into (14a) and (14b), and recognizing that the element nodal values of the partial pressures, p_{ox_i} and p_{co_i} , as well as the temporal derivatives, $\partial p_{ox_i} / \partial t$ and $\partial p_{co_i} / \partial t$, are not functions of the spatial variables, equations (14a) and (14b) may be written in the matrix form

$$\begin{bmatrix} \mathbf{COX} & 0 \\ 0 & \mathbf{CCO} \end{bmatrix} \frac{d}{dt} \begin{Bmatrix} p_{ox_j} \\ p_{co_j} \end{Bmatrix} + \begin{bmatrix} \mathbf{KOX} & \mathbf{KXC} \\ \mathbf{KCX} & \mathbf{KCO} \end{bmatrix} \begin{Bmatrix} p_{ox_j} \\ p_{co_j} \end{Bmatrix} = \begin{Bmatrix} \mathbf{FOX} \\ \mathbf{FCO} \end{Bmatrix} \quad (17)$$

where

$$(\mathbf{COX})_{ij} = \phi \frac{M_{ox}}{R\hat{T}} \int_{D^e} N_i N_j dD^e \quad (18a)$$

$$(\mathbf{CCO})_{ij} = \phi \frac{M_{co}}{R\hat{T}} \int_{D^e} N_i N_j dD^e \quad (18b)$$

$$(\mathbf{KOX})_{ij} = \frac{\hat{\rho}_{ox}^p}{\hat{\mu}_g} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\mathbf{k}} \cdot \underline{\nabla} N_j dD^e + D_{AB} \frac{M_{ox}}{R\hat{T}} \frac{\hat{p}_{co}}{\hat{p}} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\boldsymbol{\Phi}}^A \cdot \underline{\nabla} N_j dD^e \quad (18c)$$

$$(\mathbf{KXC})_{ij} = \frac{\hat{\rho}_{ox}^p}{\hat{\mu}_g} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\mathbf{k}} \cdot \underline{\nabla} N_j dD^e - D_{AB} \frac{M_{ox}}{R\hat{T}} \frac{\hat{p}_{ox}}{\hat{p}} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\boldsymbol{\Phi}}^A \cdot \underline{\nabla} N_j dD^e \quad (18d)$$

$$(\mathbf{KCX})_{ij} = \frac{\hat{\rho}_{co}^p}{\hat{\mu}_g} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\mathbf{k}} \cdot \underline{\nabla} N_j dD^e - D_{AB} \frac{M_{co}}{R\hat{T}} \frac{\hat{p}_{co}}{\hat{p}} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\boldsymbol{\Phi}}^A \cdot \underline{\nabla} N_j dD^e \quad (18e)$$

$$(\mathbf{KCO})_{ij} = \frac{\hat{\rho}_{co}^p}{\hat{\mu}_g} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\mathbf{k}} \cdot \underline{\nabla} N_j dD^e + D_{AB} \frac{M_{co}}{R\hat{T}} \frac{\hat{p}_{ox}}{\hat{p}} \int_{D^e} \underline{\nabla} N_i \cdot \underline{\boldsymbol{\Phi}}^A \cdot \underline{\nabla} N_j dD^e \quad (18f)$$

$$\begin{aligned} (\mathbf{FOX})_i &= N_1 \frac{M_{ox}}{M_c} \int_{D^e} N_i N_j \left(\Re_{cf_j} + \Re_{pc_j} \right) dD^e + \phi \frac{\hat{\rho}_{ox}^p}{\hat{T}} \frac{dT}{dt} \int_{D^e} N_i dD^e \\ &\quad - \oint_{\Gamma^e} N_i \underline{\mathbf{J}}_{ox} \cdot \underline{n} d\Gamma^e \end{aligned} \quad (18g)$$

$$\begin{aligned}
(\mathbf{FCO})_i = & -N_2 \frac{M_{co}}{M_c} \int_{D^e} N_i N_j \left(\mathfrak{R}_{cfj} + \mathfrak{R}_{pcj} \right) dD^e + \phi \frac{\hat{\rho}_{co}^p}{\hat{T}} \frac{dT}{dt} \int_{D^e} N_i dD^e \\
& - \oint_{\Gamma^e} N_i \mathbf{J}_{co} \cdot \underline{n} d\Gamma^e
\end{aligned} \tag{18h}$$

and where the symbol (^) above the quantity denotes the element average value of that quantity.

We can represent equation (17) more concisely as

$$[\mathbf{C}]_n \frac{d}{dt} \{P\}_n + [\mathbf{K}]_n \{P\}_n = \{\mathbf{F}\}_n \tag{19}$$

where $\{P\}$ represents the solution vector $\{p_{ox_i}, p_{co_i}\}^T$ and where the subscript n indicates the matrices and vectors at time t_n . Using the Backwards Difference Method (Burnett, 1987), we have for the time rate of change of the partial pressure vector

$$\frac{d\{P\}_n}{dt} = \frac{\{P\}_n - \{P\}_{n-1}}{\Delta t_n} \tag{20}$$

where $\Delta t_n = t_n - t_{n-1}$. Substituting (20), we may rewrite (19) in the simple matrix form

$$[\mathbf{K}_{eff}]_n \{P\}_n = \{\mathbf{F}_{eff}\}_n \tag{21}$$

where

$$[\mathbf{K}_{eff}]_n = \frac{1}{\Delta t_n} [\mathbf{C}]_n + [\mathbf{K}]_n \tag{22a}$$

and

$$\{\mathbf{F}_{eff}\}_n = \frac{1}{\Delta t_n} [\mathbf{C}]_n \{P\}_{n-1} + \{\mathbf{F}\}_n \tag{22b}$$

Thus, the partial pressures p_{ox} and p_{co} at each node are determined by the solution of equation (21) at each time step. The effective stiffness matrix $[\mathbf{K}_{eff}]_n$ and effective force vector $\{\mathbf{F}_{eff}\}_n$ for time t_n are calculated using equations (18), (22a) and (22b) and the partial pressure values determined at the previous time step, t_{n-1} . A flow chart illustrating the steps involved in the numerical solution routine is shown in fig. 2.

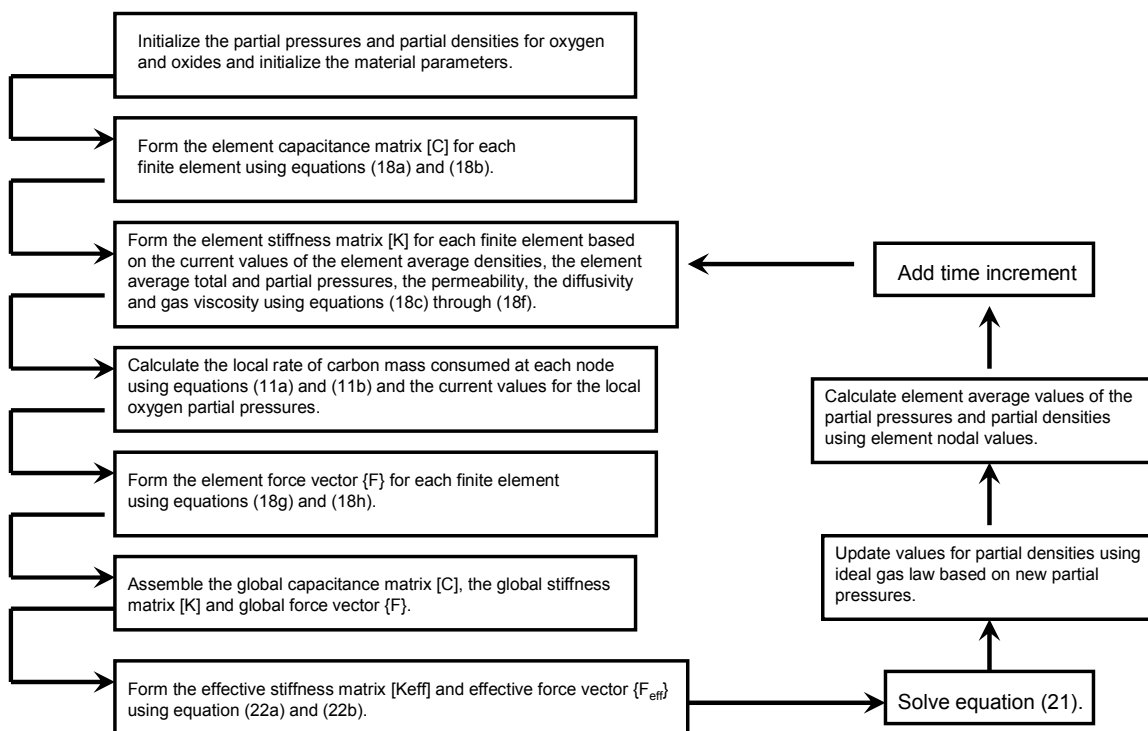


Fig. 2.—Flow Chart Showing the Steps Involved in the Numerical Solution Routine.

Discussion

In this study, a mathematical theory and an accompanying numerical scheme have been developed for predicting the oxidation behavior of C/SiC composite structures. The theory is derived from the mechanics of the flow of ideal gases through a porous solid. Within the mathematical formulation, two diffusion mechanisms are possible: (1) the relative diffusion of one species with respect to the mixture, which is concentration gradient driven and (2) the diffusion associated with the average velocity of the gas mixture, which is total gas pressure gradient driven. The result of the theoretical formulation is a set of two coupled nonlinear differential equations written in terms of the oxidant and oxide partial pressures. The differential equations must be solved simultaneously to obtain the partial vapor pressures of the oxidant and oxides as a function of space and time. The local rate of carbon oxidation is determined as a function of space and time using the map of the local oxidant partial vapor pressure along with the Arrhenius rate equation. The nonlinear differential equations are cast into matrix equations by applying the Bubnov-Galerkin weighted residual method, allowing for the solution of the differential equations numerically. The Backward Difference Method has been employed as the time marching scheme. As the differential equations are nonlinear they must be linearized within the finite element formulation. The nonlinear differential equations are linearized within each time step and solved over the time domain in a piecewise linear manner. This is achieved by continuously updating the system stiffness matrix and system force vector based on the values of the solution variables determined

in the previous time step. The end result is a numerical scheme capable of determining the variation of the local carbon oxidation rates as a function of space and time for any arbitrary C/SiC composite structure.

The difference between the modeling approach proposed here and those mentioned previously is that the current method uses a continuum mechanics approach to modeling the oxidation process in C/SiC composites. This allows for the determination of the carbon oxidation rate and carbon volume fraction distributions on a global level for any arbitrarily-shaped C/SiC component. Furthermore, the current approach includes an additional diffusion mechanism which is driven by total gas pressure gradients. This approach will predict a significantly different diffusion behavior (and consequently a different oxidation pattern) than an approach that neglects the Darcy flow mechanism whenever the total pressure gradients become significant. One instance where total pressure gradients may be significant is in C/SiC structures where high thermal gradients are present and during transient heating conditions. Finally, the current approach allows for a transient solution to the diffusion equation, whereas the previous methods used only a steady-state diffusion solution. Obviously, the current approach is a significant improvement in this regard, as the diffusion conditions present in an oxidizing C/SiC composite are almost always transient.

References

- Bathe, K.J., *Finite Element Procedures in Engineering Analysis*, Prentice-Hall Inc., Englewood Cliffs, NJ, 1982.
- Bird, Stewart, and Lightfoot, *Transport Phenomena*, Wiley, New York, NY, 1960.
- Burnett, D.S., *Finite Element Analysis: From Concepts to Applications*, Addison-Wesley Publishing Company, 1987.
- Darcy, H., "Les Fontaines Publiques de la ville de Dijon," Dalmont, Paris, 1856.
- Eckel, A.J., Cawley, J.D., and Parthasarathy, T. A., "Oxidation Kinetics of a Continuous Carbon Phase in a Nonreactive Matrix," *J. Am. Ceram. Soc.*, **78**, [4], 972–980, (1995).
- Gulbransen, E.A., Andrew, K.F., and Brassart, F.A., "The Oxidation of Graphite at Temperatures of 600 °C to 1500 °C and at Pressures of 2 to 76 Torr of Oxygen," *Journal of the Electrochemical Society*, pp. 476, June 1963.
- Halbig, M.C., "The Oxidation Kinetics of Continuous Carbon Fibers in a Cracked Ceramic Matrix Composite," NASA/TM—2001-210520, June 2001.
- Lamouroux, F., Bourrat, X., and Nasalain, R., "Structure/Oxidation Behavior Relationship in the Carbonaceous Constituents of 2D-C/PyC/SiC Composites," *Carbon*, Vol. 31, No. 8, pp. 1273–1288, 1993.
- Medford, J.E., "Prediction of Oxidation Performance of Reinforced Carbon-Carbon Material for Space Shuttle Leading Edges," presented at the AIAA 10th Thermophysics Conference, Denver, CO, May 27–29, 1975.
- Walker, P.L. Jr., Rusinko, F., Jr., and Austin, L.G., "Gas Reactions of Carbon," in *Advances in Catalysis and Related Subjects*, Vol. XI, Academic Press, Inc., New York and London, 1959.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE November 2003		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE A Model for the Oxidation of C/SiC Composite Structures			5. FUNDING NUMBERS WBS-22-706-85-04	
6. AUTHOR(S) Roy M. Sullivan				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-14244	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2003-212720	
11. SUPPLEMENTARY NOTES Responsible person, Roy M. Sullivan, organization code 5920, 216-433-3249.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Categories: 24, 27, 34, and 64 Distribution: Nonstandard Available electronically at http://gltrs.grc.nasa.gov This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A mathematical theory and an accompanying numerical scheme have been developed for predicting the oxidation behavior of C/SiC composite structures. The theory is derived from the mechanics of the flow of ideal gases through a porous solid. Within the mathematical formulation, two diffusion mechanisms are possible: (1) the relative diffusion of one species with respect to the mixture, which is concentration gradient driven and (2) the diffusion associated with the average velocity of the gas mixture, which is total gas pressure gradient driven. The result of the theoretical formulation is a set of two coupled nonlinear differential equations written in terms of the oxidant and oxide partial pressures. The differential equations must be solved simultaneously to obtain the partial vapor pressures of the oxidant and oxides as a function of space and time. The local rate of carbon oxidation is determined as a function of space and time using the map of the local oxidant partial vapor pressure along with the Arrhenius rate equation. The nonlinear differential equations are cast into matrix equations by applying the Bubnov-Galerkin weighted residual method, allowing for the solution of the differential equations numerically. The end result is a numerical scheme capable of determining the variation of the local carbon oxidation rates as a function of space and time for any arbitrary C/SiC composite structures.				
14. SUBJECT TERMS Carbon silicon carbide composites; Oxidation; Porous media; Finite element method			15. NUMBER OF PAGES 21	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	